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| (54) Title: PROCESS FOR RECOVERY OF GOLD AND/OR SILVER | | | |
| (57) Abstract Processes for the recovery of gold and/or silver from lixiviant solutions include a preliminary step of: (a) contacting the lixiviant solution with ion exchange resins containing amine functionality, optionally dispersed or distributed within a polyurethane matrix and/or in the presence of an alcohol that is substantially insoluble in the lixiviant solution, or (b) contacting the lixiviant solution with a liquid extractant in the presence of an alcohol that is substantially insoluble in the lixiviant solution. The ion exchange resin or extractant, once loaded with silver and/or gold, is then separated from the lixiviant solution, and eluted to recover the gold and/or silver values. | | | |

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PROCESS FOR RECOVERY OF GOLD AND/OR SILVER

The present invention relates to a process for recovery of gold and/or silver thiosulphate
5 from solutions and slurries and also to the use of ion exchange materials for conducting gold
and/or silver thiosulphate recovery.

Hydrometallurgical extraction of precious metals is commonly performed using
oxygenated alkaline cyanide-containing solutions, and in particular, by the use of sodium cyanide.
10 Because cyanide solutions are highly toxic and can cause environmental problems, the use of this
lixiviant is falling into disfavour. Destruction of residual cyanide by processes such as the Inco
SO₂/Air process can destroy the cyanide in tailings waters, but this represents an additional
financial cost to the mining operation. Furthermore, this process does not destroy toxic
thiocyanates which are generated by the cyanide ion reacting with sulphide minerals when these
15 minerals are present in the ore.

In many gold-containing ores, the gold can be intimately associated with sulphidic minerals
such as pyrite, pyrrhotite, arsenopyrite, marcasite, chalcopyrite, chalcocite, bornite, enargite, etc.
The gold present in association with these sulphide minerals often cannot be economically
20 recovered using cyanide without the ore being given a pretreatment such as roasting, pressure
oxidation or bacterial oxidation.

Copper, either as native copper or copper-based minerals or manganese when present in
ores leads to high reagent usage, generally poor gold recovery, and the possible discharge of
25 stable, highly toxic copper cyanide species into tailings dams. This high reagent usage can lead
to the gold recovery being uneconomic. Furthermore, the presence of copper cyanide in the
tailings discharge has led to significant bird-kills and to the banning of gold mining in areas close
to bird habitats.

30 Furthermore, carbonaceous matter can also be present in gold-containing ores and its
presence during a carbon-in-pulp (CIP) or carbon-in-leach (CIL) cyanidation-recovery process

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can lead to the loss of gold due to preg robbing. Preg robbing may be simply described as the adsorption of gold cyanide onto the surface of any material the particle size of which is smaller than the screen size used to recover the gold cyanide-loaded activated carbon from the CIP/CIL circuit. Thus, the preg robbed gold is not recovered from the circuit and is lost to tailings. The
5 complex carbonaceous materials may comprise long-chain hydrocarbons and organic acids, such as humic acids. They have been reported to vary in both their physical and chemical forms and to vary from one ore body to the next. Many procedures have been proposed to treat the carbonaceous material to minimise gold cyanide losses. Processes such as the addition of a blanking agent such as kerosene or sodium lauryl sulphate as a pretreatment; acidic or alkaline
10 pressure oxidation; roasting (including roasting of the entire ore body); removal of the carbonaceous matter by flotation; chemical oxidation as taught by Clough et al. in U.S. Patent 4,801,329 and including aqueous chlorination and nitric acid oxidation; and bacterial oxidation as suggested by Brierley et al. in U.S. Patent 5,127,942 have been adopted or researched by industry.

15

A number of other lixiviants for gold such as halides (chlorine, bromine and iodine), thiourea, nitriles (malononitrile, lactonitrile), thiocyanates, ammonia, sodium polysulphide and sodium sulphite have been proposed for the treatment of these ores. Other than chlorine, little commercial use has been made of these alternative lixiviants.

20

In U.S. Patent 4,070,182, Genik-Sas-Berezowsky et al. describes a process whereby gold could be recovered from copper-containing ores by the use of an oxygenated ammonium thiosulphate solution in the presence of ammonia and copper ions as a secondary leach for the recovery of silver and gold. In this process, the gold-thiosulphate solution is separated from the
25 solid ore residue and is then passed to a cementation process in which zinc dust is used to cause precipitation of the silver and the gold. The gold and silver then is recovered by conventional methods.

Kerley, Jr. in U.S. Patent 4,269,622 describes a process whereby an ammonium
30 thiosulphate solution containing copper, and sufficient ammonia to maintain a pH of at least 7.5 and at least 0.05% sulphite ion are combined provide a better stability of the thiosulphate radical

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can be used as a suitable lixiviant for difficult-to-treat ores, particularly those containing manganese. The proposed reaction temperature is between 40-60°C and preferably, 50-60°C. Recovery of the gold from the leach liquor was by the use of metallic zinc, iron or copper for cementation; by electrolysis; or by the addition of soluble sulphides to recover a gold sulphide
5 precipitate.

In U.S. Patent 4,654,078 Kerley, Jr. describes a process whereby the thiosulphate is produced by an in-situ chemical reaction using only elemental sulphur as the raw material, the other principal reagents, ammonia and copper, being recycled for reuse with only very small
10 amounts of make-up being required. Again, the procedure for gold recovery was as he had previously described in U.S. Patent 4,269,622.

Perez et al. in U.S. Patent 4,654,078 describes the application of the methods proposed by Kerley, Jr. to ores containing manganese and/or copper failed in commercial practice, despite
15 extensive consultation with the inventor, Mr. Kerley. The process described by Perez requires a minimum pH of 9.5 and preferably 10.0-10.5 to be maintained in the lixiviant solution to inhibit the chemical reaction caused by the presence of substantial amounts of metallic iron that result from the grinding of the ore in a ball mill prior to the lixiviating step. At pHs lower than 9.5, iron will be dissolved into the lixiviating solution destroying the copper-ammonium thiosulphate
20 complex and forming the tetrathionate complex. The tetrathionate ion has no lixiviating action on either gold or silver. Perez teaches that the pregnant solution containing the gold and silver thiosulphate anions may be separated from the leached solids and the precious metals are then recovered by conventional precipitation methods using zinc, iron, metallic copper or soluble sulphides. Copper cement was the preferred metal for this cementation step.

25

According to Wan et al. in U.S. Patent 5,354,359 refractory carbonaceous ores containing precious metals can be treated using thiosulphates at pHs of at least about 9 without the need for any additional pretreatment principally because gold thiosulphate will not load onto carbon. This inability of carbon to adsorb gold thiosulphate had previously been reported by Gallagher
30 et al. in J. Electrochem. Soc. (1989), 136(9), 2546-2551. Wan et al. proposed that thiosulphate-based lixivants can be used as an alternative lixiviant to cyanide to leach gold and

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- silver in the well-established heap leaching process. Precious metal values were preferably recovered from the lixiviant solution by precipitation with copper, zinc, aluminium or soluble sulphides. Wan et al. in Research and development activities for the recovery of gold from noncyanide solutions, In: Hydrometallurgy Fundamentals, Technology and Innovations, Eds. J.B. Hiskey and G.W. Warren, SME, Littleton, Colo. (1993), 415-436, reported that anion exchange resins are unlikely to be suitable for the recovery of gold thiosulphate except possibly from very dilute thiosulphate concentrations and that the concentrations of thiosulphate in gold-leaching systems would be too high for recovery by this technique.
- 10 The pressure oxidation of refractory carbonaceous ores containing sulphidic minerals and having preg robbing characteristics prior to thiosulphate dissolution of the gold contained therein, has been disclosed by Marchbank et al. in U.S. Patent 5,536,297. Pressure oxidation may be conducted under hot acidic conditions as disclosed by Thomas et al. in U.S. Patent 5,071,477 or under hot alkaline conditions as disclosed by Mason et al. in U.S. Patent 4,522,589. The
15 oxidised ore slurry is then leached at a temperature between 40 and 55°C, a pH of between 7 and 8.7, and in a stirred tank reactor. Gold is recovered from the gold-bearing leachate by cementation on zinc, copper or iron; or following the addition of ammonia to prevent copper cyanide formation, cyanide is then added to produce an aurocyanide anion with its subsequent adsorption on a suitable adsorbent, preferably activated carbon; or cyanide and adsorbent is
20 added to the last thiosulphate leach tank and the aurocyanide recovered in a co-current operation. The gold cyanide is stripped from the activated carbon using a hot alkaline cyanide solution. Alternatively, the pregnant solution may be separated from the leached solids and the gold thiosulphate then recovered using either a suitable ion exchange resin or a suitable solvent extractant.
- 25 Gold in a refractory sulphide mineral has been recovered by oxidation of the sulphide mineral with a chromolithotropic bacteria followed by leaching using a slightly alkaline solution containing amino acids of microbial origin and thiosulphate as the gold-complexing agent [Groudev et al. Two-stage microbial leaching of a refractory gold-bearing pyrite ore, Miner. Eng.
30 (1996), 9(7), 707-713]. These researchers suggest that the presence of the amino acids did not change the rate of dissolution but served to reduce the overall thiosulphate consumption.

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The recovery of platinum group elements (PGEs), gold and silver from playa-evaporite sediments with a hot, highly caustic sodium thiosulphate leach liquor has been disclosed by Groves et al. in U.S. patent 5,405,430. The presence of sodium sulphite in the lixiviant is said to act as a solvent on the host jarosites in the way that gypsum is soluble in sodium thiosulphate solutions. After filtration, the pregnant solution is subjected to a selective precipitation process to recover the precious metals. Lead acetate at about 60°C is recommended for the precipitation of gold from the pregnant solution.

10 The recovery of gold thiosulphate from solutions and from pulps has been conducted using zinc or copper metal in a cementation process. This requires a solid-liquid separation of the pregnant gold thiosulphate solution from the leached solid residue, thereby introducing added cost into the process by the need to wash the solids with additional solution to remove any residual gold thiosulphate remaining on the solid. Furthermore, adsorption or precipitation of
15 the gold thiosulphate anion onto solids present in the slurry leads to gold-loss by preg robbing.

Activated carbon as a solid/liquid separation mechanism has been proposed to recover the gold thiosulphate in a manner similar to that of the CIP/CIL processes. Gold thiosulphate will not readily load onto activated carbon, but gold cyanide will. Therefore, in the method outlined
20 by Lulham and Lindsay in PCT/GB91/00114, (International Patent Application No. WO 91/11539) required the addition of at least a stoichiometric amount of cyanide ions to a gold thiosulphate solution and adsorption of the resultant gold complex on an adsorbent, such as activated carbon or an ion exchange resin. The cyanide addition is said to convert the gold thiosulphate into gold cyanide so that it will then load onto the sorbent. However, this chemical
25 reaction between the cyanide anion and the gold thiosulphate anion is non-discriminatory and therefore, not all of the gold thiosulphate may be converted to gold cyanide, unconverted gold thiosulphate is then lost to tailings. Furthermore, activated carbon in this recovery process is known to suffer from poor resistance to attrition, slower loading kinetics than ion exchange resins, requires thermal regeneration for reactivation, loads calcium and magnesium ions leading
30 to pore blocking, sorbs organic materials from solution leading to lower gold cyanide recovery.

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In plant pulps, contact is made by the activated carbon with silica and alumina such that the carbon can become saturated with fine slurry particles in less than three hours. It has been observed that the equilibrium loading of fines was independent of their concentration in the slurry. Furthermore, the presence of these particles inside an adsorbent decreases the effective
5 diffusion of gold complexes into the adsorbent matrix.

Ion exchange resins as an alternative to activated carbon for use as a solid/liquid separation material resin-in-pulp (RIP) process have been described as having the following advantages:

10

(a) anion exchange resins are superior to currently available activated carbon with respect to both the kinetics of loading and the equilibrium loading of gold thiosulphate;

(b) resins may be eluted at room temperature, whereas activated carbon must be eluted
15 at temperatures approaching 100°C;

(c) activated carbon requires thermal reactivation;

(d) resins do not appear to be poisoned by organic species such as flotation reagents,
20 machine oils and lubricants, solvents, etc. which have an adverse effect on carbon;

(e) resins do not load calcium carbonate to the same extent as activated carbon, and therefore do not require the same need for hydrochloric acid washing to remove precipitated calcite;

25

(f) minerals such as clays, shales, haematite, alumina, etc. can inhibit the performance of activated carbon whilst resins do not suffer from this problem to the same extent;

(g) resins do not suffer from attrition to the same extent as activated carbon. Carbon
30 losses are of the order of 10 to 50 g/tonne of ore treated, whereas resin losses are expected to be less than 10 g/tonne; and

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(h) resins are not adversely affected to the same extent by temperature as is activated carbon during the adsorption stage.

5 Ion exchange resins are manufactured in bead form generally from polystyrene-divinyl benzene, acrylic, or phenol-formaldehyde resins. Ion exchange fibres can be produced from either polyacrylonitrile onto which active ligands can be attached, or polypropylene fibres on to which polystyrene-divinylbenzene can be grafted. Ligands can then be attached to the surface of these resins or fibres by conducting one or more suitable chemical reactions. Alternatively, liquids
10 which exhibit ion exchanging properties (generally referred to as "solvent extractants") may be imbibed or impregnated into certain of these polymers.

The resins evaluated for gold cyanide recovery have had several disadvantages, including, small particle size to provide a large surface-to-volume ratio, lower selectivity for gold over
15 other base-metal cyanides prevalent in leach liquors, and pK_a values which prevent the resin loading gold cyanide at pH values above 10. While a number of resins have been trialed for gold cyanide recovery, no resins have been identified which are able to be satisfactorily used for the recovery of gold thiosulphate. The loading of gold thiosulphate onto commercially available ion exchange resins is considered to be too low for industrial applications.

20

We have now found that gold and/or silver thiosulphate may be recovered from solution by the use of a polyurethane matrix having ion exchange resin with an amine functionality dispersed or distributed throughout said polyurethane matrix.

25 According to the present invention there is provided a process for the extraction of gold and/or silver thiosulphates from solution comprising the steps of:

(a) contacting a gold thiosulphate and/or silver thiosulphate containing lixiviant solution with a polyurethane matrix having ion exchange resin with an amine
30 functionality dispersed or distributed throughout said polyurethane matrix to load said polyurethane matrix with gold thiosulphate and/or silver thiosulphate;

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(b) separating the loaded polyurethane matrix; and

(c) recovering the gold and/or silver values by elution from the polyurethane matrix.

5

Advantageously, we have also found that the process described above is surprisingly improved by contacting the lixiviant solution with the polyurethane matrix in the presence of a water-insoluble alcohol. Accordingly in a preferred embodiment there is provided a process for
10 the extraction of gold and/or silver thiosulphates from solution comprising the steps of:

(a) contacting a gold thiosulphate and/or silver thiosulphate containing lixiviant solution with a polyurethane matrix having ion exchange resin with an amine functionality dispersed or distributed throughout said polyurethane matrix in the
15 presence of an alcohol, said alcohol being substantially insoluble in said lixiviant solution to load said polyurethane matrix with gold thiosulphate and/or silver thiosulphate;

(b) separating the loaded polyurethane matrix; and

20

(c) recovering the gold and/or silver values by elution from the polyurethane matrix.

We have further found that the surprising improvements found by contacting the lixiviant
25 solution with the ion exchange material in the presence of a water-insoluble alcohol apply not only to polyurethane matrices in which an ion exchange resin is distributed or dispersed but to ion exchange resins generally, including ion exchange beads, such as those used in prior art processes. According to a second aspect there is provided a process for the extraction of gold and/or silver thiosulphates from solution comprising the steps of:

30

(a) contacting a gold thiosulphate and/or silver thiosulphate containing lixiviant

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solution with an ion exchange resin with an amine functionality in the presence of an alcohol, said alcohol being substantially insoluble in said lixiviant solution to load said ion exchange resin with gold thiosulphate and/or silver thiosulphate.

- 5 (b) separating the loaded ion exchange resin; and
- (c) recovering the sorbed gold and/or silver values by elution from the ion exchange resin.

10 Surprisingly, we have further found that the improvements provided by the use of a water-insoluble alcohol may also be obtained in liquid/liquid extractions. According to a third aspect there is provided a process for the extraction of gold and/or silver thiosulphates from solution comprising the steps of:

- 15 (a) contacting a gold thiosulphate and/or silver thiosulphate containing lixiviant solution with a liquid extractant blend, said liquid extractant blend comprising a organic extractant and an alcohol, said liquid extractant blend being substantially immiscible in said lixiviant solution to load the organic extractant with gold thiosulphate and/or silver thiosulphate;
- 20 (b) separating the loaded liquid extractant blend; and
- (c) recovering the gold and/or silver values from the loaded liquid extractant blend.

The process of the present invention may be conducted by any convenient means. The
25 solution and/or silver thiosulphate may be contacted with the ion exchange resin or liquid extractant by any convenient means known to those skilled in the art which will depend on the form of the ion exchange resin or liquid extractant used. We have found it preferable to maintain the gold and/or silver thiosulphate solution at an alkaline pH. The loaded ion exchange resin or liquid extractant may be separated from the solution by any convenient means which will
30 depend on the form of the ion exchange resin or liquid extractant used.

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The recovery of the gold thiosulphate and/or silver thiosulphate may be carried out by any convenient means. Stripping of the ion exchange resin or liquid extractant of the invention maybe accomplished by a suitable solvent such as sodium or ammonium thiocyanate, often containing dimethyl formamide, acidified thiourea, zinc cyanide, or in some instances, pH control
5 by stripping at a pH in excess of 12 and if required, in the added presence of sodium benzoate.

It has surprisingly been found that when the ion exchange resins are dispersed or distributed throughout a polyurethane matrix, as is described in PCT/AU93/00312 and PCT/AU94/00793 and the ion exchange resins are provided with an amine functionality that
10 superior extraction results are achieved. The particularly superior results were not expected from a review of the prior art.

Polyurethane resins are noted for their abrasion and chemical resistance. These resins can be produced as beads, or as fibres, but in particular, they may be expanded to form foams with
15 the cellular properties varying from a microcellular expanded product to highly expanded foams with a density of 10 kg/m^3 . By the correct selection of polyols, blowing agents and cell control agents these cells may be closed or open. In an open celled product, most of the cell windows are removed during production to leave only the struts behind. If a more open cellular product is desired, then the polyurethane foam can be further improved by "reticulation", a mechanism
20 well-known to those skilled in the production of polyurethane foams. Furthermore, if desired, particles including metal powders, metal alloy particles, inorganic materials (such as barytes), metal oxides (such as magnetite or ferrosilicon) may be added to the polyurethane to modify its final density and if required, to assist in recovery of the resin from the aqueous solutions or pulps.

25

The polyurethane matrix in which the ion exchange resin is distributed or dispersed offers exceptional abrasion resistance, and resistance to osmotic shock. These polyurethane resins can be formed into particles of a size such that they can be readily recovered from gold thiosulphate and/or silver thiosulphate circuits. This particle size may be significantly larger than for
30 conventional ion exchange resins. As previously noted, conventional ion exchange resins require a small particle size to enable them to have sufficient exchange capacity. Conventional resins are

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also generally made macro reticular to increase their capacity. It has been reported that this process may lead to pores being generated in the ion exchange resin which can block and reduce its capacity to remove metal ions from solution. The polyurethane matrix may be reticulated open cell foam through which the lixiviant is passed.

5

The polyurethane matrix has an ion exchange resin with amine functionality dispersed or distributed throughout the matrix. The term "dispersed or distributed" when used herein includes a dispersion of discrete particles as well as networks of polymers which are incorporated onto or into the surfaces, external and internal, of the polyurethane matrix such as in
10 interpenetrating polymer systems.

The amine functionality may preferably be provided by a second polymer, polymerised on the external and/or internal surfaces of the polyurethane matrix. The polyurethane resins can be interpenetrated with a second polymer during, or subsequent to production. Such an
15 interpenetration may be by the formation of a polystyrene-divinyl benzene resin, polyacrylonitrile, polyacrylates, or other desired polymer. Alternatively, this second polymer maybe formed in the polyol prior to the polyurethane resin production.

This second polymer may then be further reacted by such chemical modifications as
20 chloromethylation. The polyurethane foam containing chloromethylated sites may then undergo a further chemical modification such as amination to provide the amine functionality.

As a further embodiment, chloromethylstyrene may be substituted for polystyrene and therefore, an interpenetrated polyurethane resin containing chloromethylated polystyrene,
25 crosslinked with divinyl benzene or other suitable monomer maybe produced. This resin may then undergo further chemical modification such as amination to provide the amine functionality.

Monomers, particularly reactive monomers, such as hydroxyethyl methacrylate, octene diol, hexene 1,2 diol, polybutadiene diol may be incorporated into the polyurethane during its
30 manufacture to provide reactive unsaturated sites in the cured polyurethane. One or more different unsaturated monomers may then be interpenetrated into the cured polyurethane and

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polymerised. The resultant polymer is thus chemically bound to the polyurethane matrix. Vinylpyridine, 1-vinylimidazole, diallyldimethylammonium chloride, [3-(methacryloylamino)propyl] trimethylammonium chloride, styrylguanidine, are examples of such monomers containing an unsaturated functional group. Whilst it is preferred that the monomer(s) or blend of monomer(s) and comonomer(s) be interpenetrated into a polyurethane matrix containing an unsaturated group it is not a requirement of the invention that such reactive site should be present in the polyurethane matrix.

The interpenetrated polyurethane containing a suitable ligand may be induced to undergo a further chemical reaction such as alkylation. For example, a polyurethane may be interpenetrated with a second polymer such as vinylpyridine (possibly in the presence of comonomer such as divinylbenzene) and then the pyridine site could be methylated by reaction with a methyl halide.

Copolymer polyols may be produced by the grafting polymerisation of unsaturated monomers on to poly(ethylene oxide) (EO) or poly(propylene oxide) (PO) or mixed EO-PO containing polyols. Typical monomers would include vinyl pyridine, 1-vinylimidazole, [3-(methacryloylamino)propyl]-trimethylammonium chloride. This polymer polyol may then be incorporated as a raw material in the manufacture of a polyurethane. It is also possible for specific polymers to be induced to undergo further chemical reactions.

In a preferred embodiment of the present invention polyurethane foams incorporate polystyrene-divinyl benzene. The benzene ring is preferably then chloromethylated. Following this reaction, a further reaction may desirably be conducted in which amine functional groups are incorporated into the polyurethane foam. Varying lengths of alkyl chain have been incorporated. Dimethylamine, trimethylamine, triethylamine, tributylamine, dimethylethanolamine, are typical of such alkylamines.

In a further modification, a desired ligand can be incorporated into the polyurethane by reacting it with a diisocyanate to form a prepolymer or adduct, and this prepolymer incorporated into the polyurethane. Depending upon the particular isocyanate selected and/or the particular

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properties of the polyurethane produced, so the isocyanate prepolymer may be induced to react with the amide groups and any free hydroxyl groups present in the polyurethane resin.

Alternatively, a selected diisocyanate monomer such as hexamethylene diisocyanate (HDI) or isocyanate-terminated prepolymer may be reacted with amide groups or unreacted hydroxyl groups or both amide and hydroxyl groups present in a polyurethane polymer. Desired ligands can then be reacted with the unreacted isocyanate groups.

Any suitable amine functionality may be introduced such as by amination. Suitable amine functionality may be provided by alkylamines wherein the alkyl chain is between 1 and 6 carbon atoms long, or which can be reacted to form an imidazoline ligand, or which may be a guanidine, pyridine, quinoline, pyrrolidine, diallylamine, dibenzylamine, or other suitable amine including heterocyclic amines. It is particularly preferred that the amine functionality is provided by a quaternary amine such quaternary amines are preferably alkyl or mixed alkyl trimethyl ammonium salts, including dodecyl, tetradecyl and hexadecyl. One or more methyl groups may be replaced with alkyl groups containing from 2 to 16 carbon atoms and/or substituted or non-substituted aromatic ring structures including benzyl, naphthenyl, cyclohexyl or heterocyclic groups.

In the second aspect of the present invention a wide variety of known ion exchange resins may be made far more effective by contacting the lixiviant solution with the ion exchange resin in the presence of a water-insoluble alcohol. Such ion exchange resins include anion exchange resins having amine functionality, preferably a strong base resin consisting of a quaternary amine attached to a polymer backbone (e.g. polystyrene beads). A strong base resin is preferred over a weak base resin because while a strong base resin's effectiveness is not dependent on environmental pH, a weak base resin typically requires an environmental pH of less than, or about 7. The capacity of a typical strong base resin is also greater than that of a weak base resin, such that a lower volume of resin is required. Furthermore, because strong base resins are more widely used, they are typically more available and economical than weak base resins. Gel resins and macroporous resins are both suitable, with macroporous resins being preferred because they are more durable and because the resin is not subjected to significant variations in pH in this process which, if it were the case, would call for gel resins over macroporous resins. The

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preferred resin comprises beads of at least about 0.8 mm in average diameter to facilitate screening. Suitable resins include all commercial strong-base resins of either Type I (triethylamine functional groups) or Type II (triethyl ethanolamine functional groups), particularly those that are based on a macroporous matrix of polystyrene, cross-linked with 8-10% divinyl benzene. Specific strong-base ion exchange resins for use in this invention include Dowex M-41 and Dowex-MSA-1 (Type I), Dowex M-42, Dowex MSA-2 (Type II), Dowex-SBR, Dowex M-41 which are manufactured by Dow Chemical, Amberlite IRA-900C, Amberlite IRA-904 (Type I), and Amberlite IRA-910 (Type II), which are manufactured by Rohm & Haas. Also satisfactory are the Lewaitit M-600 resins. MP 500, which is manufactured by Bayer, and the gel-type resin 21K, manufactured by Dow Chemical. A suitable weak-base resin is A7, available from Rohm & Haas.

Various guanidine functional groups may also be introduced into the polyurethane foam. For example, guanidine, di-o-tolyl guanidine, di-n-alkylguanidine, N-(6-aminohexyl)-N'-butyl guanidine, are examples of such ligands. This includes for example guanidine complexes such as disclosed in GB 2 186 563A, in U.S. Patents 4,814,007, 4,895,597, 4,992,200, 5,028,259, 5,198,021, 5,340,380, WO 93/19,212, WO 97/10,367 or as disclosed in ZA89/2733 which are specifically incorporated by reference.

Other amine functionality introduced includes pyridine, quinoline, benzylamine, dibenzylamine, pyrrolidine, diallylamine, aminodiacetate, amino phosphonic acids.

In a further preferred embodiment, polyacrylonitrile is incorporated into the polyurethane foam. Amine functionality is then preferably introduced into the polymer. For example, diethylenetriamine and ethylenediamine have been reacted with the nitrile group introduced into the polyurethane foam. By the selection of reaction conditions, so imidazoline groups may be formed.

Epoxy resins may be dissolved in a suitable solvent and blended with aliphatic amines such as DETA (diethylene triamine), TETA (triethylene tetramine), poly(oxypropylene triamine) and the like and interpenetrated into the polyurethane matrix and cured.

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Lewis-base modifiers, such as alkyl phosphorus esters, trialkyl phosphate, dialkyl alkyl phosphonate, alkyl dialkylphosphinate, trialkyl phosphine oxides, sulphones, and sulphoxides, may be combined with the amine-based extractants to further modify the extractability of these organic complexes. The inductive effects of the alkyl chains and solvation of the amine or amine salt is believed to increase the availability of the nitrogen electron pair, which in turn encourages protonation of the amine. High temperature and low ionic strength may inhibit solvation extraction.

10 In the preferred embodiment of the present invention the ion exchange resin is contacted with the lixiviant solution in the presence of an alcohol which is substantially insoluble in the lixiviant solution. It will be understood that the term alcohol also includes phenols and organic molecules containing the -OH moiety. It will be understood that the term "substantially insoluble" means the alcohol is insoluble in the lixiviant solution although a small or insignificant amount of the alcohol may dissolve in the lixiviant solution. Suitable alcohols include n-pentanol, 15 n-hexanol, 2-ethylhexanol, isodecanol, dodecanol, tridecanol, hexadecanol, octadecanol; phenols such as heptylphenol, octylphenol, nonylphenol and dodecylphenol. Preferably the alcohol is a non-aromatic alcohol. The preferred non-aromatic alcohols include pentanol and tridecanol.

20 In the process of the present invention where liquid extractant blend is used it is preferable that the molar ratio of organic extractant to water insoluble alcohol is in the range of from 1:100 to 100:1. The preferred ratio being 1:3. In a further preferred embodiment it is preferable that the water-insoluble alcohol consist of a non-aromatic alcohol or mixture thereof. In this embodiment any aromatic alcohol present in the liquid extractant blend is to be considered 25 part of the organic extractant for the purposes of calculating the molar ratio. Any inert carriers such as macro reticular polystyrene-divinyl benzene is to be disregarded when determining the molar ratio.

In the process of the present invention the amount of alcohol relative to any ion exchange resin is preferably in range of from 10% to 300% by weight of the ion exchange resin

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The present invention is particularly suitable for the extraction of gold and/or silver thiosulphates from solutions. The process may be used to extract gold thiosulphate from a gold thiosulphate containing solution which is part of a pulp or slurry.

5 It should be noted that the application of the insoluble alcohol is not restricted to the recovery of gold thiosulphate only. Other gold complexes such as the gold halides, particularly chloride and bromide, gold thiourea, gold amine, gold cyanide, gold thiocyanate may also benefit from the use of an insoluble alcohol.

10 In the process of the third aspect of the present invention a liquid extractant blend is employed for the extraction of gold and/or silver thiosulphate from solution. The liquid extractant blend comprises an organic extractant and an alcohol wherein the liquid extractant blend is substantially insoluble in the lixiviant solution. Optionally, the liquid extractant blend may include an organic solvent.

15 Suitable organic extractants contain amine functionality and include trioctylamine, guanidine functionality, tri-(C₈-C₁₀)alkyl methyl ammonium chloride, and particularly trimethyl hexadecyl ammonium chloride, or other extractant, including phosphine oxides, sulphones, sulphoxides, tri(2-ethyl hexyl) phosphate, tributylphosphate and dibutyl butyl phosphonate.

20 Preferably the organic extractant is trimethyl hexadecyl ammonium chloride.

The substantially insoluble alcohols referred to herein may be blended with the organic extractant to form the liquid extractant blend. A wide variety of essentially water-immiscible hydrocarbon solvents may be used in the liquid extractant blend. Suitable hydrocarbon solvents

25 include aliphatic and aromatic hydrocarbons. Preferably the hydrocarbon solvents will be essentially chemically inert and have flash points in excess of 60°C. The preferred hydrocarbon solvent is a narrow cut kerosene.

The liquid extractant blend, may advantageously be impregnated or imbibed into an ion

30 exchange resin or be incorporated into a suitable non-reactive carrier. Such non-reactive carriers may include activated carbon, a polymer in a suitable form such as macro-reticular

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polystyrene-divinyl benzene, acrylate, polyvinyl alcohol, polyvinyl chloride, polyurethane, was (including paraffin wax, bees wax) which is insoluble in the water-insoluble alcohol. Such carrier would generally be in particulate bead-form and preferably contains a large internal void volume. Internal voidage is generally obtained by adding a suitable porogen or porogen mixture during the bead polymerisation step. These impregnated polymers may also be incorporated into the polyurethane matrix incorporating ion exchange functionality, such as foam during its manufacture.

The incorporation of these extractants into a polyurethane matrix can be modified by either pre- or post-incorporation of a diisocyanate or a diisocyanate prepolymer onto the polyurethane foam and curing it such as by passing steam through the isocyanate-impregnated polyurethane foam containing the organic extractant. Alternatively, the organic extractant may be blended with the diisocyanate component (providing that the organic reactant does not react with the diisocyanate) to form a solid product prior to its incorporation onto the polyurethane foam.

The ion exchange resins for use in the present invention are also capable of impregnation with liquid extractant blends which are able to increase the removal of gold and/or silver thiosulphate anions from the lixiviant solution.

The lixiviant solutions may be clarified, such as is normally obtained in gold heap leaching operations. Lixiviant solutions may also be obtained from pulps, such as occur in carbon-in-pulp, carbon-in-leach, resin-in-pulp or resin-in-leach processes.

In the well-established heap leaching process for gold recovery, clarified gold-containing solutions are generated. Furthermore, if a solid/liquid separation step is included in the gold lixiviation circuit, clarified gold-containing solutions are obtained. Gold thiosulphate when present in these clarified solutions may be recovered by the application of solvent extraction technology. In this process, gold thiosulphate present in the aqueous phase is contacted with a suitable amine which may be dispersed in a substantially water-insoluble organic carrier fluid. The gold thiosulphate will then transfer from the aqueous phase to the organic phase. After a suitable

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contact time, phase disengagement followed by phase separation is allowed to occur. The gold thiosulphate which has transferred into the organic phase is then stripped by again contacting the organic phase with a suitable aqueous stripping solution. The gold is then recovered from the stripped solution by any suitable method such as reduction, precipitation, cementation or
5 electrowinning. The method outlined will be clearly evident to those who are skilled in the use of solvent extraction technology.

The impregnated resins and polyurethane-based polymers may optionally be used to recover the gold thiosulphate from these same pregnant heap leach solutions. The gold
10 thiosulphate so recovered may then be eluted from these solid sorbents in the manner previously disclosed.

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", or variations such as "comprises" or "comprising", will be
15 understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

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EXAMPLES

EXAMPLE 1:

5 100 ml of an aqueous solution containing 10 ppm of gold as the thiosulphate anion was prepared using a 0.005M sodium thiosulphate. The initial solution pH was adjusted using ammonia and was then contacted for 5 minutes with 10 ml of an organic solution prepared as follows:

(a) 5 g/l of a 28.5% active aqueous solution of trimethyl hexadecyl ammonium chloride
10 (APS Specialties Quatramine C16/29) in pentanol.

(b) 5 g/l of Aliquat 336 in pentanol.

15 The following extractions (in g/l) were obtained:

| | pH 8 | pH 9 | pH 10 |
|----------------|------|------|-------|
| Extractant (a) | 10.4 | 16.4 | 15.0 |
| Extractant (b) | 12.8 | 16.0 | 10.6 |

20

EXAMPLE 2.

100 ml of an aqueous solution containing 5 ppm of gold thiosulphate was contacted for 5 minutes with 10 ml of an organic solution prepared as follows:

25

(a) 5 g/l of a 28.5% active aqueous solution of trimethyl hexadecyl ammonium chloride
(APS Specialties Quatramine C16/29) in pentanol.

30 (b) 5 g/l of Aliquat 336 in pentanol.

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The following extractions (in g/l) were obtained:

| | pH 8 | pH 9 | pH 10 |
|------------------|------|------|-------|
| Extractant (a) | 2.4 | 7.4 | 5.6 |
| 5 Extractant (b) | 8.8 | 8.4 | 8.2 |

EXAMPLE 3:

100 ml of an aqueous solution containing 10.2 ppm of gold thiosulphate plus 1M ammonium
 10 thiosulphate at pH 10 was contacted for 5 minutes with 10 ml of an organic solution prepared
 as follows:

(a) 5 g/l of a 28.5% active aqueous solution of trimethyl hexadecyl ammonium chloride
 (APS Specialties Quatramine C16/29) in pentanol.

15

(b) 5 g/l of Aliquat 336 in pentanol.

The following extractions (in g/l) were obtained:

| | |
|-------------------|-----|
| 20 Extractant (a) | 2.8 |
| Extractant (b) | 0.6 |

EXAMPLE 4.

100 ml of an aqueous solution containing 10.2 ppm of gold thiosulphate plus 1M ammonium
 25 thiosulphate plus 1M sodium thiosulphate at pH 10 was contacted for 5 minutes with 10 ml of
 an organic solution prepared as follows:

(a) 5 g/l of a 28.5% active aqueous solution of trimethyl hexadecyl ammonium chloride
 (APS Specialties Quatramine C16/29) in pentanol.

30

(b) 5 g/l of Aliquat 336 in pentanol.

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The following extractions (in g/l) were obtained:

Extractant (a) 7.8

Extractant (b) 5.6

5

EXAMPLE 5.

Extractant (a) as for Examples 1, 2, 3 and 4 was blended in the ratio 1:3 with pentanol and then impregnated into the following polymers:

10

XAD 7 (hydrophilic bead)*

XAD 16 (hydrophobic bead)* (* Product of Rohm & Haas)

15 Activated carbon

Reticulated polyurethane foam

20 Each of the above impregnated polymers were then contacted at room temperature with 100 ml of a solution containing 10.2 ppm gold thiosulphate in 0.005M sodium thiosulphate adjusted to an initial pH of 10 for 2 hours. The following loadings of gold thiosulphate were obtained:

50 mg of impregnated XAD 7 (hydrophilic bead) loaded

19.8 g Au/kg of impregnated polymer,

25

50 mg of impregnated XAD 16 (hydrophobic bead) loaded

20.0 g Au/kg of impregnated polymer,

100 mg of impregnated activated carbon loaded 0.5 g Au/kg of impregnated carbon,

100 mg of an impregnated and reticulated polyurethane foam loaded 5.4 g Au/kg of impregnated polyurethane foam.

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The poor loading of the gold thiosulphate onto activated carbon supports the opportunity to recover gold thiosulphate from ores containing carbonaceous matter.

EXAMPLE 6.

- 5 100 ml of an aqueous solution containing 10 ppm of gold as the thiosulphate anion was prepared using a 0.005M sodium thiosulphate. The initial solution pH was adjusted using ammonia and was then contacted at room temperature with 0.1 of a solid prepared by the polymerisation of diallyl amine. After 6 hours the resin was found to have loaded 4900 mg of gold/ kg of polymer.

10 EXAMPLE

- (a) A DMAPMA-BA (N[3-(dimethylamino) propyl] methacrylamide-butyl acrylate) modified polymer was interpenetrated into a polyurethane foam.
- 15 (b) An epoxy-DETA (diethylene triamine) blend was interpenetrated into a polyurethane foam.

Both foams were then contacted at room temperature with a solution containing 10.4 ppm gold thiosulphate in 0.2 M sodium thiosulphate adjusted to an initial pH of 7.5 for 2 hours.

20

Polymer (a) loaded 2.7 g Au/kg modified polyurethane foam,

Polymer (b) loaded 1.2 g Au/kg modified polyurethane foam,

EXAMPLE

- 25 An aqueous solution containing 10.3 ppm of gold thiosulphate plus 0.2 M sodium thiosulphate at pH 9 was contacted for 5 minutes with an equal volume of an organic extractant containing 10% of Aliquat 336 in toluene. 4.9 g Au/l organic was obtained

EXAMPLE

30

IRA 400, a strong-base ion exchange resin manufactured by Rohm and Haas, activated carbon,

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impregnated with 45.6% of Aliquat 336, a reticulated polyurethane foam, impregnated with 155% of Aliquat 336, were each separately contacted with an aqueous solution containing 10 ppm gold thiosulphate plus 0.5 M sodium thiosulphate adjusted to pH 10 for 2 hours at room temperature. The following loadings were obtained:

5

| | |
|---------------------------------|------------------------|
| IRA 400 | 1.1 g Au/kg polymer, |
| Activated carbon + Aliquat 336 | 0.056 g Au/kg product, |
| Polyurethane foam + Aliquat 336 | 1.3 g Au/kg product. |

10 EXAMPLE

100 ml of an aqueous solution containing 10.5 ppm of gold as the thiosulphate anion was prepared using 0.005 M sodium thiosulphate. The pH of the solution was adjusted to 10 using ammonia and then contacted for 5 minutes with 10 ml of an organic solution prepared as follows:

(a) 5g/l of a 28.5% active aqueous solution of trimethyl hexadecyl ammonium chloride in a 1:1 mixture of nonylphenol and Shellsol 2046.

(b) 5g/l of Aliquat 336 in a 1:1 mixture of nonylphenol and Shellsol 2046.

(c) 5 g/l of Alamine 336 (a tertiary amine manufactured by Henkel Corporation) in a 1:1 mixture on nonylphenol and Shellsol 2046.

(d) 5 g/l of Primene JMT (a primary amine manufactured by Rohm and Haas) in a 1:1 mixture of nonylphenol and Shellsol 2046.

(e) 5 g/l of Primene JMT (a primary amine manufactured by Rohm and Haas) plus 5 g/l tributylphosphate in a 1:1 mixture of nonylphenol and Shellsol 2046.

EXAMPLE

100 ml of an aqueous solution containing 10.7 ppm of gold thiosulphate anion was prepared using 0.005M sodium thiosulphate. The pH of the solution was adjusted using ammonia and then contacted for 5 minutes with 10 ml of an organic solution prepared as follows:

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- (a) 5 g/l of a active aqueous solution of trimethyl hexadecyl ammonium chloride in pentanol.
- (b) 5 g/l of Aliquat 336 in pentanol.
- 5 (c) 5g/l of Alamine 336 (a tertiary amine manufactured by Henkel Corporation) in pentanol.
- (d) 5 g/l of Primene JMT (a primary amine manufactured by Rohm and Haas) in pentanol.
- (e) 5 g/l of Primene JMT (a primary amine manufactured by Rohm and Haas) plus 5 g/l
10 tributylphosphate in pentanol.

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be
15 understood that the invention includes all such variations and modifications which fall within its spirit and scope. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in this specification, individually or collectively, and any
and all combinations of any two or more of said steps or features.

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CLAIMS

1. A process for the extraction of gold and/or silver thiosulphates from solution comprising the steps of:

5

(a) contacting a gold thiosulphate and/or silver thiosulphate containing lixiviant solution with a polyurethane matrix having ion exchange resin with an amine functionality dispersed or distributed throughout said polyurethane matrix to load said polyurethane matrix with gold thiosulphate and/or silver thiosulphate;

10

(b) separating the loaded polyurethane matrix; and

(c) recovering the gold and/or silver values by elution from the polyurethane matrix.

15 2. A process according to claim 1 wherein the polyurethane matrix is an expanded polyurethane foam

3. A process according to either claim 1 or claim 2 wherein the polyurethane matrix is a reticulated polyurethane foam

20

4. A process according to any one of claims 1 to 3 wherein the amine functionality is provided by a second polymer polymerised on the external and/or internal surfaces of the polyurethane matrix.

25 5. A process according to any one of claims 1 to 4 wherein second polymer is polystyrene-divinyl benzene having amine functionality subsequently reacted onto the second polymer.

6. A process according to any one of claims 1 to 4 wherein second polymer is
30 polyacrylonitrile having amine functionality subsequently reacted onto the second polymer.

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7. A process according to any one of claims 1 to 4 wherein second polymer is an epoxy resin may be dissolved in a suitable solvent and blended with aliphatic amines such as DETA (diethylene triamine), TETA (triethylene tetramine), poly(oxypropylene triamine) and interpenetrated into the polyurethane matrix and cured.

5

8. A process according to any one of claims 1 to 7 wherein an organic extractant is impregnated in the polyurethane matrix.

9. A process according to claim 8 wherein the organic extractant contains amine
10 functionality and is selected from the group consisting of trioctylamine, guanidines, tri-(C₈-C₁₀)alkyl methyl ammonium chloride, trimethyl hexadecyl ammonium chloride, phosphine oxides, sulphones, sulphoxides, tri(2-ethyl hexyl phosphate, tributylphosphate and dibutyl butyl phosphonate.

15 10. A process according to either claim 8 or claim 9 wherein the organic extractant is trimethyl hexadecyl ammonium chloride.

11. A process according to any one of claims 1 to 7 wherein the the organic extractant is blended with a water-immiscible hydrocarbon solvent.

20

12. A process for the extraction of gold and/or silver thiosulphates from solution comprising the steps of:

(a) contacting a gold thiosulphate and/or silver thiosulphate containing lixiviant
25 solution with a polyurethane matrix having ion exchange resin with an amine functionality dispersed or distributed throughout said polyurethane matrix in the presence of an alcohol, said alcohol being substantially insoluble in said lixiviant solution to load said polyurethane matrix with gold thiosulphate and/or silver thiosulphate;

30

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(b) separating the loaded polyurethane matrix; and

(c) recovering the gold and/or silver values by elution from the polyurethane matrix.

5 13. A process according to claim 12 wherein the substantially water-insoluble alcohol is selected from the group consisting of n-pentanol, n-hexanol, 2-ethylhexanol, isodecanol, dodecanol, tridecanol, hexadecanol, octadecanol; phenols such as heptylphenol, octylphenol, nonylphenol and dodecylphenol.

10 14. A process according to either claim 12 or claim 13 wherein the substantially water-insoluble alcohol is a non-aromatic alcohol.

15 15. A process according to any one of claims 12 to 14 wherein the non-aromatic alcohol is selected from the group consisting of n-pentanol and tridecanol.

16. A process according to any one of claims 12 to 15 wherein the amount of alcohol relative to any ion exchange resin is preferably in range of from 10% to 300% by weight of the ion exchange resin.

20 17. A process according to any one of claims 12 to 16 wherein the polyurethane matrix is an expanded polyurethane foam

18. A process according to any one of claims 12 to 17 wherein the polyurethane matrix is a reticulated polyurethane foam

25 19. A process according to any one of claims 12 to 18 wherein the amine functionality is provided by a second polymer polymerised on the external and/or internal surfaces of the polyurethane matrix.

30 20. A process according to any one of claims 12 to 19 wherein second polymer is

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polystyrene-divinyl benzene having amine functionality subsequently reacted onto the second polymer.

21. A process according to any one of claims 12 to 20 wherein second polymer is
5 polyacrylonitrile having amine functionality subsequently reacted onto the second polymer.

22. A process according to any one of claims 12 to 21 wherein second polymer is an
epoxy resin may be dissolved in a suitable solvent and blended with aliphatic amines such
as DETA (diethylene triamine), TETA (triethylene tetramine), poly(oxypropylene triamine)
10 and interpenetrated into the polyurethane matrix and cured.

23. A process according to any one of claims 12 to 22 wherein an organic extractant is
impregnated in the polyurethane matrix.

15 24. A process according to claim 23 wherein the organic extractant contains amine
functionality and is selected from the group consisting of trioctylamine, guanidines,
tri-(C₈-C₁₀)alkyl methyl ammonium chloride, trimethyl hexadecyl ammonium chloride,
phosphine oxides, sulphones, sulfoxides, tri(2-ethyl hexyl phosphate, tributylphosphate and
dibutyl butyl phosphonate.

20

25. A process according to either claim 23 or claim 24 wherein the organic extractant
is trimethyl hexadecyl ammonium chloride.

26. A process according to any one of claims 12 to 25 wherein the the organic extractant
25 is blended with a water-immiscible hydrocarbon solvent.

27. A process for the extraction of gold and/or silver thiosulphates from solution
comprising the steps of:

30 (a) contacting a gold thiosulphate and/or silver thiosulphate containing lixiviant

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solution with an ion exchange resin with an amine functionality in the presence of an alcohol, said alcohol being substantially insoluble in said lixiviant solution to load said ion exchange resin with gold thiosulphate and/or silver thiosulphate.

5 (b) separating the loaded ion exchange resin; and

(c) recovering the sorbed gold and/or silver values by elution from the ion exchange resin.

10 28. A process according to claim 27 wherein the substantially water-insoluble alcohol is selected from the group consisting of n-pentanol, n-hexanol, 2-ethylhexanol, isodecanol, dodecanol, tridecanol, hexadecanol, octadecanol; phenols such as heptylphenol, octylphenol, nonylphenol and dodecylphenol.

15 29. A process according to either claim 27 or claim 28 wherein the substantially water-insoluble alcohol is a non-aromatic alcohol.

30. A process according to any one of claims 27 to 29 wherein the non-aromatic alcohol is selected from the group consisting of n-pentanol and tridecanol.

20

31. A process according to any one of claims 27 to 30 wherein the amount of alcohol relative to any ion exchange resin is preferably in range of from 10% to 300% by weight of the ion exchange resin.

25 32. A process according to any one of claims 27 to 31 wherein an organic extractant is impregnated in the ion exchange resin.

33. A process according to claim 32 wherein the organic extractant contains amine functionality and is selected from the group consisting of trioctylamine, guanidines,
30 tri-(C₈-C₁₀)alkyl methyl ammonium chloride, trimethyl hexadecyl ammonium chloride,

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phosphine oxides, sulphones, sulphoxides, tri(2-ethyl hexyl phosphate, tributylphosphate and dibutyl butyl phosphonate.

34. A process according to either claim 32 or claim 33 wherein the organic extractant
5 is trimethyl hexadecyl ammonium chloride.

35. A process according to any one of claims 32 to 34 wherein the the organic extractant
is blended with a water-immiscible hydrocarbon solvent.

10 36. A process according to any one of claims 27 to 35 wherein the ion exchange resin is
an anion exchange resins having amine functionality.

37. A process according to any one of claims 27 to 36 wherein the ion exchange resin is
a strong base resin consisting of a quaternary amine attached to a polymer backbone.

15

38. A process for the extraction of gold and/or silver thiosulphates from solution
comprising the steps of:

20 (a) contacting a gold thiosulphate and/or silver thiosulphate containing lixiviant
solution with a liquid extractant blend, said liquid extractant blend comprising a
organic extractant and an alcohol, said liquid extractant blend being substantially
immiscible in said lixiviant solution to load the organic extractant with gold
thiosulphate and/or silver thiosulphate;

25 (b) separating the loaded liquid extractant blend; and

(c) recovering the gold and/or silver values from the loaded liquid extractant blend.

39. A process according to claim 38 wherein the substantially water-insoluble alcohol is
30 selected from the group consisting of n-pentanol, n-hexanol, 2-ethylhexanol, isodecanol,

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dodecanol, tridecanol, hexadecanol, octadecanol; phenols such as heptylphenol, octylphenol, nonylphenol and dodecylphenol.

40. A process according to either claim 38 or claim 39 wherein the substantially water-
5 insoluble alcohol is a non-aromatic alcohol.

41. A process according to any one of claims 38 to 40 wherein the non-aromatic alcohol is selected from the group consisting of n-pentanol and tridecanol.

10 42. A process according to any one of claims 38 to 41 wherein the molar ratio of organic extractant to water insoluble alcohol is in the range of from 1:100 to 100:1.

43. A process according to any one of claims 38 to 42 wherein the molar ratio of organic extractant to water insoluble alcohol is 1:3.

15

44. A process according to any one of claims 38 to 43 wherein the liquid extractant blend is impregnated or imbibed into a suitable non-reactive carrier.

45. A process according to claim 44 wherein the non-reactive carrier is selected from the
20 group consisting of activated carbon, a polymer in the form of a macro-reticular polystyrene-divinyl benzene, acrylate, polyvinyl alcohol, polyvinyl chloride, polyurethane, wax (including paraffin wax, bees wax) which is insoluble in the water-insoluble alcohol.

46. A process according to either claim 44 or claim 45 wherein the non-reactive carrier
25 is in particulate bead-form and contains a large internal void volume. Internal voidage.

47. A process according to any one of claims 38 to 46 wherein an organic extractant is impregnated in the ion exchange resin.

30 48. A process according to claim 47 wherein the organic extractant contains amine

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functionality and is selected from the group consisting of trioctylamine, guanidines, tri-(C₈-C₁₀)alkyl methyl ammonium chloride, trimethyl hexadecyl ammonium chloride, phosphine oxides, sulphones, sulphoxides, tri(2-ethyl hexyl phosphate, tributylphosphate and dibutyl butyl phosphonate.

5

49. A process according to either claim 47 or claim 48 wherein the organic extractant is trimethyl hexadecyl ammonium chloride.

50. A process according to any one of claims 47 to 49 wherein the organic extractant is
10 blended with a water-immiscible hydrocarbon solvent.

51. A process according to any one of claims 1 to 50 wherein the gold and/or silver thiosulphate solution is maintained at an alkaline pH.

15 52. A process according to any one of claims 1 to 50 wherein the process is applied to other gold complexes selected from the group consisting of gold halides, gold chloride and gold bromide, gold thiourea, gold amine, gold cyanide, gold thiocyanate.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU 98/00722

| | | |
|---|--|--|
| A. CLASSIFICATION OF SUBJECT MATTER | | |
| Int Cl ⁶ : C22B 11/00, 3/42, 3/40, B01D 11/04, B01J 39/18, 39/04 | | |
| According to International Patent Classification (IPC) or to both national classification and IPC | | |
| B. FIELDS SEARCHED | | |
| Minimum documentation searched (classification system followed by classification symbols) IDC: Int.Cl.6 C22B 3/40, 3/42, 11/00, B01D 11/04, B01J 39/04, 39/18 | | |
| Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched | | |
| Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Derwent Online, class C22B, B01D and B01J with keyword, (thiosulphate or thiosulfate) and (silver or gold or au or ag), period 1975-98 | | |
| C. DOCUMENTS CONSIDERED TO BE RELEVANT | | |
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| P, X | WO 97/49474 A (HENKEL CORPORATION) 31 December 1997. See abstract | 1-52 |
| X | WO 95/18159 A (MONTECH PTY LTD et al) 6 July 1995. See abstract. | 1-11 |
| X | WO 88/04696 A (STENSTRÖM) 30 June 1988. See abstract, page 3 lines 29-33. | 38-43 |
| <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex | | |
| <p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> | | |
| Date of the actual completion of the international search 14 October 1998 | | Date of mailing of the international search report 26 OCT 1998 |
| Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (02) 6285 3929 | | Authorized officer Graeme Broxam Telephone No.: (02) 6283 2133 |

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU 98/00722

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|---|--|-----------------------|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| Y | WO 96/28251 A (MONTECH PTY LTD et al.) 19 September 1996. See abstract, examples. | 1-52 |
| Y | WO 94/00237 A (MONASH UNIVERSITY) 6 January 1994. See abstract, examples. | 1-52 |

INTERNATIONAL SEARCH REPORT

International application No.

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Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See attached.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims
2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.

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Box II

The independent claims do not share a common special technical feature and are consequently not so linked as to form a single inventive concept.

The special technical feature of claim 1 is a process in which the gold and/or silver ions contained in a solution of gold and/or silver thiosulphate are extracted using an ion exchange resin with amine functionality combined with a polyurethane matrix.

The special technical feature of claim 12 is similar to that of claims 1 except that an alcohol that is substantially insoluble in the lixiviant solution is necessarily present.

The special technical feature of claim 27 is similar to that of claim 12 except that the ion exchange resin need not be combined with a polyurethane matrix.

The common special technical feature of claims 1, 12 and 27 can be seen to be a process in which the gold and/or silver ions contained in a solution of gold and/or silver thiosulphate are extracted using as ion exchange resin with amine functionality. This is already known, with reference to the citations raised in this report, and *a posteriori* the claims lack unity of invention.

Claim 38 relates to an entirely different invention to that of the previous groups of claims. It is directed to a process in which the gold and/or silver thiosulphate are extracted using liquid (not resin) extractant, not limited to amine functionality, in conjunction with an alcohol that is substantially insoluble in the lixiviant solution.

INTERNATIONAL SEARCH REPORT **Information on patent family members**

International application No.
PCT/AU 98/00722

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

| Patent Document Cited in Search Report | | | | Patent Family Member | | | |
|--|----------|----|----------|----------------------|---------|----|--------------|
| WO | 97/49474 | AU | 31375/97 | | | | |
| WO | 95/18159 | AU | 13757/95 | NZ | 278304 | ZA | 9410325 |
| WO | 88/04696 | SE | 8605371 | | | | |
| WO | 96/28251 | AU | 48710/96 | CA | 2217866 | EP | 814907 |
| WO | 94/00237 | AU | 43000/93 | EP | 647160 | NZ | 252953 |
| | | ZA | 9304593 | | | | |
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